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(54) Title: NOVEL POLYURETHANE FOAM COMPOSITION HAVING IMPROVED FLEX FATIGUE (57) Abstract The present invention relates to a process for preparing a flexible polyurethane foam from the reaction of a polyisocyanate composition prepared from the reaction of an excess of organic polyisocyanate and a polyether polyol having a high ethylene oxide content and an isocyanate reactive composition comprising a chain extending agent and a combination of a polyether polyol having a high ethylene oxide content and a random copolymer having a high ethylene oxide content, and the product prepared therefrom.		

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NOVEL POLYURETHANE FOAM COMPOSITION
HAVING IMPROVED FLEX FATIGUE

1 FIELD OF THE INVENTION

The present invention relates to a water
blown integral skin polyurethane foam prepared from an
5 organic polyisocyanate and two polyether polyols
having a high ethylene oxide content in
synergistically effective amounts, to an isocyanate-
reaction system useful in preparing such foams, and to
10 the process of preparing the same.

BACKGROUND OF THE INVENTION

Elastomeric polyurethane foams for
applications, such as for example, shoe soles,
15 desirably exhibit good physical properties including
abrasion resistance, flexibility and durability.
Typically, these foams are prepared by reacting an
organic isocyanate with a substance having at least
one isocyanate reactive group in the presence of a
20 catalyst, blowing agent and a variety of optional
additives. The reaction is generally carried out in a
mold whereby a higher density skin forms at the
interface of the reaction mixture and the inner
surface of the mold.

25 At the present time, one of the most common
types of blowing agents utilized in the preparation of
such polyurethane foams are the chlorofluorocarbons
(CFCs), e.g., freon-11. Shoe soles comprised of these
polyurethane foams, especially freon blown
30

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1 polyurethane foams, have a very thick skin, are
abrasion resistant, stable and exhibit excellent flex
fatigue properties.

5 However, since industry is faced with a
mandate to reduce and eventually eliminate the use of
CFCs due to environmental concerns, it is necessary to
find an alternative blowing agent. Water is a highly
desirable blowing agent and has been used as a blowing
agent to prepare lower density polyurethane foams.

10 However, heretofore, water has been found to be
generally unacceptable as the sole blowing agent,
especially in the preparation of foams intended for
use as shoe soles. The density of the polyurethane
foams prepared utilizing water as the sole blowing
15 agent is generally too low to provide the adequate
stability and cushioning demanded for modern shoes.
In addition, shoe soles comprised of water blown
polyurethane foams do not have thick skin and exhibit
very poor flex fatigue properties. Thus, the shoe
20 soles crack very easily after several flexing
operations.

The present inventor, however, has
successfully found a reaction system for preparing an
all water-blown microcellular integral skin
25 polyurethane foam and has thus overcome the problems
described hereinabove. More specifically, utilizing
the reaction system of the present invention, the
polyurethane foam prepared therefrom has improved flex
fatigue properties, making it an ideal material for
30 use in shoe sole compositions. The inventor has found

- 1 that improved flex properties are realized if the
isocyanate reaction component contains a mixture of
two high ethylene oxide containing polyols.

5 SUMMARY OF THE INVENTION

Accordingly, the present invention is directed to an integral skin polyurethane foam prepared by contacting under effective reaction conditions a polyisocyanate composition with an
10 isocyanate reactive composition in the presence of water as the sole blowing agent characterized in that:

(a) the polyisocyanate composition has a free NCO value of about 15% to about 25% and comprises an isocyanate-terminated prepolymer which is the
15 reaction product of an excess of an organic polyisocyanate and a first ethylene oxide capped polyether polyol having an average nominal hydroxyl functionality of 2-6, an equivalent weight ranging from about 700 to about 5000 and an ethylene oxide
20 content of at least 25% by weight, at least about 50% by weight of the total ethylene oxide groups present being capped on said polyether polyol;

(b) the isocyanate reactive composition comprises about 6% to about 12.5% (w/w) of a chain
25 extending agent and a combination of a second ethylene oxide capped polyether polyol and a random copolymer of ethylene oxide and propylene oxide in synergistically effective amounts to form said polyurethane foam, said second ethylene oxide capped
30 polyol having an average nominal hydroxyl

1 functionality of 2-3, an equivalent weight ranging
from about 700 to about 5,000, and an ethylene oxide
content of at least about 25% by weight, with at least
about 50% by weight of the total ethylene oxide groups
5 present being capped on the polyether polyol ethylene
oxide, and said copolymer having an average nominal
hydroxyl functionality of 2-3, an equivalent weight
ranging from about 700 to about 5,000 and an ethylene
oxide content of at least about 65% by weight; and
10 (c) water as a blowing agent is present in
an amount effective to provide the resulting polymer
with a density ranging from about 0.1 to about 1.1
specific gravity, wherein the weight ratio of water to
the chain extending agent ranges from about 0.01 to
15 about 0.20. In a preferred embodiment, about 10 to
about 250 parts by weight of the isocyanate reactive
composition is reacted per 100 parts by weight of the
polyisocyanate composition:

The present invention is further directed to
20 a reaction system comprising the polyisocyanate
composition and the isocyanate reactive composition
described hereinabove, and water wherein the weight
ratio of the water to the chain extending agent ranges
from about 0.01 to about 0.20. In a preferred
25 embodiment, the weight ratio of the isocyanate
reactive composition to the polyisocyanate composition
ranges from about 0.1 to about 2.5.

Further the present invention is concerned
with a process for preparing the polyurethane foam
30 described hereinabove.

1 BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts a shoe sole design identified herein as Style A comprised of the polyurethane foam of the present invention.

5 Figure 2 depicts a shoe sole design identified herein as Style B comprised of the polyurethane foam of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

10 An aspect of the present invention is directed to an integral skin polyurethane foam prepared from an isocyanate reactive composition containing a combination of high ethylene oxide-containing polyols. More specifically, one polyol is
15 a ethylene oxide capped polyether polyol which has an ethylene oxide content of at least greater than 25% wherein at least 50% and more preferably at least 75% thereof by weight is at the end of the polymer chain. The other polyol is a random copolymer of ethylene
20 oxide and propylene oxide having an ethylene oxide content of at least about 65% by weight. These two polyols act in a synergistic manner, and when reacted with a chain extending agent form an isocyanate reactive composition which when reacted with the
25 polyisocyanate composition of the present invention in the presence of water forms a polyurethane foam with a flexible integral skin having excellent abrasion resistance and an enhanced resistance to cracking on flex. The polymer skin of the polyurethane foam
30 produced in accordance with the present invention

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1 possesses sufficient tensile modulus and elongation
and tear strength to survive a 90 to 180 degree bend
without exhibiting surface cracks. It is thus ideal
for use in shoe sole applications as well as for other
5 molded articles.

As used herein, the term "isocyanate index"
or "NCO-index" or "index" is the ratio of NCO groups
over isocyanate-reactive hydrogen containing groups
present in a formulation, given as a percentage with
10 respect to the amount of isocyanate theoretically
required for reacting with the amount of isocyanate-
reactive hydrogen containing groups used in a
formulation:

$$\text{NCO index} = \frac{[\text{NCO}] \times 100\%}{[\text{active hydrogen-containing groups}]}$$

In other words, the NCO index expresses the
percentage of isocyanates actually used in a
formulation. Therefore, an index of 100% represents a
20 1:1 ratio of NCO equivalents to isocyanate-reactive
groups.

It should be observed that the isocyanate
index as used herein is considered from the point of
view of the actual foaming process involving the
25 isocyanate composition and the isocyanate-reactive
composition. Any isocyanate groups consumed in a
preliminary step to produce the prepolymer or other
modified polyisocyanate or any active hydrogens
reacted with isocyanate to produce modified polyols or
30 polymers are not taken into account in the calculation

1 of the isocyanate index. Only the free isocyanate
groups and the free isocyanate-reactive hydrogen
containing groups (including those of the water)
present at the actual foam forming stage are taken
5 into account.

The expression "isocyanate-reactive
hydrogen-containing groups" as used herein for the
purpose of calculating the isocyanate index refers to
the total number of hydroxyl and amine groups present
10 in the reactive compositions in the form of polyols,
polyamines and/or water; this means that for the
purpose of calculating the isocyanate index in the
actual foaming process, one hydroxyl group is
considered to comprise one reactive hydrogen and one
15 water molecule is considered to comprise two active
hydrogens. Primary and secondary amine groups are
each considered to contain one (available) isocyanate
reactive hydrogen for the purposes of calculating the
index.

20 "Polyurethane foam" refers to cellular
products as obtained by reacting polyisocyanate with
the isocyanate reactive composition using foaming
agents, and, in particular, includes cellular products
obtained with water as a reactive foaming agent
25 (involving a reaction of water with isocyanate groups
yielding urea linkages and carbon dioxide and
producing polyurea-urethane foams).

The term "polyisocyanate composition" is to
be construed as including mixtures of isocyanate-
30 terminated prepolymers and free polyisocyanates. Such

1 free polyisocyanates may have been added to the prepolymer as well, provided the free NCO value of the polyisocyanate composition remains at the level as indicated hereinabove.

5 The term "reaction system" refers to a combination of ingredients wherein the polyisocyanate composition is kept in a container separate from the isocyanate-reactive ingredients.

"Average nominal hydroxyl functionality" is
10 used herein to indicate the number average functionality (number of hydroxyl groups per molecule) of the individual polyether polyol ingredients on the assumption that this is the number average functionality (number of active hydrogen atoms per
15 molecule) of the initiator(s) used in their preparation, although in practice it will often be somewhat less because of some terminal unsaturation.

As used herein it is to be understood, unless indicated to the contrary, that any term in the
20 plural, also includes the singular and vice versa.

As indicated hereinabove, the polyurethane foams are prepared according to the process of the present invention by intimately contacting under effective reaction conditions the polyisocyanate
25 composition with the isocyanate reactive composition in the presence of water as the sole blowing agent.

The polyisocyanate composition has a free NCO value of about 15% to about 25% by weight and more preferably from about 17% to about 21% by weight. As
30 described herein, it is comprised of an isocyanate-

- 1 terminated prepolymer. This prepolymer is the
reaction product of an excess of an organic
polyisocyanate and an ethylene oxide capped polyether
polyol.
- 5 The organic polyisocyanate which may be used
in the present invention include any of the aliphatic,
cycloaliphatic, araliphatic or aromatic
polyisocyanates known to those skilled in the art,
especially those that are liquid at room temperature.
- 10 Examples of suitable polyisocyanates include 1, 6-
hexamethylene diisocyanate, isophorone diisocyanate,
1, 4-cyclohexane diisocyanate, 4, 4'-
dicyclohexylmethane diisocyanate, 1,5-naphthylene
diisocyanate, 1,4-xylylene diisocyanate, 1,4-phenylene
15 diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene
diisocyanate, and the diphenylmethane diisocyanates
("MDI"), including 4,4'-diphenylmethane
diisocyanate, (4,4'-MDI), 2,4'-diphenyl methane
diisocyanate (2,4'-MDI), 2,2'-diphenyl methane
20 diisocyanate (2,2'-MDI), and polymethylene
polyphenylene polyisocyanates (polymeric MDI) and the
like. Mixtures of these polyisocyanate can also be
used. Moreover, polyisocyanate variants, i.e.,
polyisocyanates, especially MDI's, that have been
25 modified in a known manner by the introduction of
urethane, allophanate, urea, biuret, carbodiimide,
uretonimine, isocyanurate, and/or oxazolidone residues
can also be used in the present systems (hereinafter
referred to as "MDI variants" or "modified MDI").
- 30 These modified polyisocyanates are well known in the

1 art and are prepared by reactions known to the skilled
artisan. For example, the uretonimine-carbodiimide-
modified polyisocyanate is obtained by employing well-
known carbodiimide-promoting catalysts in the
5 polyisocyanate composition to convert the isocyanate
to the carbodiimide at temperatures ranging from 50°C
to 250°C., which then proceeds to react with further
unconverted polyisocyanates at room temperature to
form a uretonimine-modified polyisocyanate. Typical
10 catalysts useful in this conversion to the
uretonimine-carbodiimide modified polyisocyanates
include phospholene-1-oxides and 1-sulfides, diaza and
axaza-phospholanes and phosphorinanes, triaryl arsines
and trialkyl phosphates described in U.S. Patent Nos.
15 5,284,880 and 4,743,626, both of which are herein
incorporated by reference.

In general, aromatic polyisocyanates are
preferred for use in the present reaction system. The
most preferred aromatic polyisocyanate is
20 diphenylmethane diisocyanate (MDI), for example, the
4,4'-MDI, 2,4'-MDI, polymeric MDI, MDI variants and
mixtures thereof. By "polymeric MDI, it is meant the
polymethylene polyphenylene polyisocyanates which are
comprised in the polyisocyanate compositions and which
25 have a functionality of at least 2.5. The polymeric
MDI are commercially available and are manufactured by
the phosgenation of polyamine mixtures obtained from
the condensation of aniline and formaldehyde in
appropriate proportions. For the purpose of this
30 invention, polymeric MDI's having functionality in

- 1 this range 2.5-3.5 and preferably 2.5-3.1 are particularly suitable.

The most preferred MDI is the 4,4'-MDI or a mixture of 4,4'-MDI and 2,4'-MDI, wherein the mixture
5 comprises 4,4'-MDI in an amount greater than about 85% by weight and more preferably greater than about 90% by weight and most preferably greater than about 95% by weight. In addition, polymeric MDI may additionally be present in amounts ranging from 0.4%
10 to about 4%, based upon the total weight of isocyanate present in the polyisocyanate compositions. It is even more preferred that the organic polyisocyanate is a mixture of 4,4'-MDI and 2,4'-MDI as discussed above and a modified MDI, especially a mixture of 4,4'-MDI
15 and 2,4'-MDI and a MDI composition modified by the introduction of urethane, allophanate, urea, biuret, carbodiimide, isocyanate, oxazolidone and/or uretonimine residues. In this more preferred embodiment, it is preferred that the modified MDI be
20 present in about 5% to about 15% by weight of the total amount of isocyanate present in the polyisocyanate composition, and that the 4,4'-MDI is present in amounts greater than about 85% and more preferably greater than 90% by weight of the total
25 amount of isocyanate present in the polyisocyanate composition and that the 2,4'-MDI is present in amounts less than about 7.5% and especially less than about 5% by weight of the total amount of isocyanate present in the polyisocyanate composition. In the
30 most preferred embodiment, the organic polyisocyanate

1 consists of 4,4'-MDI, and 2,4'-MDI and a modified mixture of 4,4'-MDI and 2,4'-MDI, wherein the MDI is modified with uretonimine, in the amounts given hereinabove.

5 The polyether polyols useful for preparing the isocyanate terminated prepolymer contain at least about 25% by weight ethylene oxide groups, and more preferably about 25% to about 35% by weight ethylene oxide groups. At least 50%, and preferably at least 10 75% by weight of these ethylene oxide groups are present at the end of the polyether polyol (tipped). The polyether polyols have an average nominal functionality of 2-6, and preferably 2-4. They have a number average equivalent weight of about 700 to about 15 5,000, and a preferred equivalent weight ranging from about 1000 to about 4,000, and more preferably ranging from about 1200 to about 3500 and most preferably ranging from about 1500 to about 3000.

20 The polyether polyols which are to be used for preparing the isocyanate-terminated prepolymer include the products obtained by the polymerization of ethylene oxide with another cyclic oxide, for example, propylene oxide in the presence of polyfunctional 25 initiators; however, the product must maintain the requirements described hereinabove. Suitable initiator compounds contain a plurality of active hydrogen atoms and include water and low molecular weight polyols, for example, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, cyclohexane dimethanol, resorcinol, bisphenol 30

1 A, glycerol, trimethylolpropane, 1,2,6-hexantriol,
pentaerythritol and the like. Mixtures of initiators
and/or cyclic oxide may be used.

Especially useful polyether polyols include
5 poly(oxyethylene oxypropylene) diols and/or triols
obtained by the sequential addition of propylene and
ethylene oxides to di-or trifunctional initiators, as
fully described in the prior art. Mixtures of said
diols and triols are also useful.

10 Examples of the polyether polyol useful in
preparing the isocyanate terminated prepolymer of the
present invention include Daltocel® F-481, i.e., an EO
capped diol of equivalent wt 1870, having 27.1% EO
(remainder PO); PBA® 5181 i.e., polyether polyol
15 containing 27% EO (all tipped), MW (molecular weight)=
3750, average nominal hydroxy functional is 2; and the
like.

The isocyanate-terminated prepolymer is
prepared by the reaction of an excess amount of the
20 polyisocyanate with the polyether polyol. The amounts
of polyisocyanate and polyether polyol utilized are
those known to be effective to obtain a prepolymer
having the indicated NCO value utilizing techniques
known in the art. For example, the prepolymer may be
25 prepared by reacting the organic polyisocyanate with
the polyether polyol followed by dilution with
modified polyisocyanate, as defined herein, if
present. Alternatively, modified polyisocyanate may
be mixed with the unmodified polyisocyanate prior to
30 reaction with the polyol. Such reaction is allowed to

1 take place at effective temperatures to form the
prepolymer, such as from about 40°C to about 100°C,
and in general, the use of a catalyst, is optional.
The relative amounts of organic polyisocyanate and
5 polyol depend on the desired NCO value of the
prepolymer, the NCO value of the polyisocyanate and
the OH value of the polyol and can be easily
calculated by those skilled in the art.

At least 90% of the groups obtained from the
10 reaction of the polyisocyanate and the polyether
polyol in preparing the prepolymer are urethane
groups. To the prepolymers so prepared, low amounts
(up to 30% by weight) of polyisocyanate or a variant
thereof may be added provided the NCO value remains in
15 the indicated range described hereinabove. The amount
added is in general preferably less than about 20% by
weight based on the total weight of the polyisocyanate
composition. The added polyisocyanate or variant may
be selected from those mentioned above. Aromatic
20 polyisocyanates and, in particular, MDI based
polyisocyanates are preferred. It is even more
preferred that a modified polyisocyanate be added, and
it is even more preferred that the added
polyisocyanate be the variant of the MDI utilized in
25 reacting with the polyol.

The other major component, the isocyanate
reactive composition, comprises inter alia, a high
ethylene oxide capped polyether polyol ("second
polyol"). In fact, the general characteristics of
30 the polyol described hereinabove with respect to the

1 prepolymer is applicable to the ethylene oxide capped
polyol utilized in the isocyanate reactive
composition, with the exception that it has an average
nominal hydroxyl functionality of 2-3 and that the
5 polyol is either a triol or more preferably a diol.
Thus, for example, it has a number average equivalent
weight of about 700 to about 5,000, and a preferred
range of about 1000 to about 4000, and more preferably
ranging from about 1200 to about 3500 and most
10 preferably ranging from about 1500 to about 3000. It
contains at least about 25% by weight ethylene oxide
groups and more preferably from about 25% to about 35%
by weight of ethylene oxide groups. At least 50%, and
preferably at least 75% by weight of the ethylene
15 oxide groups are present at the end of the polyether
polyol (tipped).

It is preferred that the ethylene oxide
capped polyol utilized in the isocyanate reactive
composition be the same as that utilized in preparing
20 the prepolymer described hereinabove.

Another component of the isocyanate reactive
composition is the random copolymer of ethylene oxide
and propylene oxide. The copolymer has an average
nominal hydroxyl functionality of 2 to 4 and
25 preferably 2 to 3. Its equivalent weight ranges from
about 700 to about 5,000, and more preferably from
about 1000 to about 3000 and most preferably from
about 1200 to about 2000. This copolymer also has a
high ethylene oxide content. The ethylene oxide is
30 present in amounts greater than about 60% by weight of

1 the copolymer and more preferably ranges from about
65% by weight to about 85% by weight. The copolymers
are diols or triols of poly-(oxyethyleneoxypropylene)
polyols obtained by the sequential addition of
5 propylene and ethylene oxides to di- or trifunctional
initiators, such as glycols (e.g. ethylene glycol,
propylene glycol; diethylene glycol and the like);
cyclohexane dimethanol, resorcinol,
trimethylolpropane, 1, 2, 6-hexanetriol,
10 pentaerythritol, and the like. Mixtures of initiators
may also be utilized.

Examples of the copolymers include ARCOL[®]-
2580, i.e., a random EO/PO copolymer (having 75%
ethylene oxide initiated with trimethylolpropane) of
15 equivalent weight of 1335, and the like.

As will be explained in more detail below,
the present inventor has found that the combination of
the two types of high-EO polyether polyols in the
isocyanate reactive composition act synergistically
20 i.e., the combination of the two polyether polyols
results in an integral skin polyurethane foam having
improved and unexpected flex properties, relative to a
polyurethane foam formed with only one of these
polyether polyols present. Thus, each is present in
25 the isocyanate reactive composition in synergistic
amounts. In a preferred embodiment, the second polyol
is present in amounts ranging from about 20% to about
80% by weight of the isocyanate reactive composition
and more preferably, from about 40% to about 60% by
30 weight of the isocyanate reactive composition and most

1 preferably about 50% (w/w). On the other hand, the
copolymer is preferably present in amounts ranging
from about 1.5% to about 23% by weight of the
isocyanate reactive composition and most preferably
5 from about 2% to about 10% by weight of the isocyanate
reactive composition and most preferably at about 3%
by weight thereof.

Besides the two types of polyether polyol
indicated hereinabove, the isocyanate reactive
10 composition may additionally contain conventional
polymeric polyols, such as a polyether polyol, wherein
the ethylene oxide level is below about 25%. These
polyols have a molecular weight ranging from about
1,000 to about 10,000 and a functionality of 2-4, and
15 preferably 2-3.

Such conventional polymeric polyols have
been fully described in the prior art and include
reaction products of alkylene oxides, for example,
ethylene oxide and/or propylene oxide, with initiators
20 containing from 2 to 4 active hydrogen atoms per
molecule. Suitable processes for the preparation of
these additional polyether polyols, for example,
include those disclosed by Wurtz in 1859 (see
Encyclopedia of Chemical Technology, Vol. 7, pp. 257-
25 262, published by Interscience Publishers, Inc. (1951)
or U.S. Pat. Nos. 1,922,459 and 3,040,076, the
contents of all of which are incorporated by
reference. Generally, the alkylene oxide(s) is
polymerized at pressures above atmospheric pressure
30 with an initiator in the presence of a strongly basic

1 material such as an alkali metal hydroxide or tertiary
amine acting as an alkoxylation catalyst. Suitable
catalysts include strong bases, such as hydroxides,
e.g., potassium hydroxide and sodium hydroxide and the
5 like. Suitable initiators include low molecular
weight diols and polyols, for example glycols,
glycerol, trimethylolpropane, triethanolamine,
pentaerythritol, sorbitol and sucrose, and polyamines,
for example ethylene diamine, tolylene diamine,
10 diaminodiphenylmethane and polymethylene polyphenylene
polyamines, and aminoalcohols, for example,
ethanolamine and diethanolamine, and mixtures of such
initiators.

Other conventional polymeric polyols that
15 may be additionally present in the isocyanate reactive
composition include polyester polyols obtained by the
condensation of appropriate proportions of glycols and
higher functionality polyols with dicarboxylic acids.
Still further conventional polymeric polyols that may
20 additionally be present in the isocyanate reactive
composition include terminated polythioethers,
polyamides, polyesteramides, polycarbonates,
polyacetals, polyolefins and polysiloxanes. These
polymeric polyols are those conventionally utilized in
25 this art, and are prepared by conventional means.

The polyamines referred to hereinabove may
have a molecular weight of at least 1000, and include
amino-ended polyethers, polyesters, polyesteramides,
polycarbonates, polyacetals, polyolefins and
30 polysiloxanes.

1 The polyamines may also have a molecular
weight below 1000, and these include aliphatic,
cycloaliphatic or araliphatic polyamines containing
two or more groups, such as the low molecular weight
5 amino-ended polyethers and aromatic polyamines such as
DETDA. Suitable imino- or enamino functional
reactants include those compounds which are derived
from the modification of the above described amino-
functional compounds, e.g. upon their reaction with an
10 aldehyde or ketone.

 The polyester polyols referred to
hereinabove which may be used include
hydroxylterminated reaction products of polyhydric
alcohols such as ethylene glycol, propylene glycol,
15 diethylene glycol, 1,4-butanediol, neopentyl glycol,
1,6-hexanediol, cyclohexane dimethanol, glycerol,
trimethylpropane or polyether polyols or mixtures of
such polyhydric alcohols, and polycarboxylic acids
especially dicarboxylic acids or their ester-forming
20 derivatives, for example, succinic, glutaric and
adipic acids or their dimethyl esters, sebacic acid,
phthalic anhydride, tetrachlorophthalic anhydride or
dimethyl terephthalate or mixtures thereof.
Polyesters obtained by the polymerization of lactones,
25 for example, caprolactones, in conjunction with a
polyol or hydroxy carboxylic acids, such as hydroxy
caproic acid, may also be used.

 Polyesteramides may be obtained by the
inclusion of aminoalcohols such as ethanolamine in
30 polyesterification mixtures.

1 The polythioether polyols which may be used
include products obtained by condensing thiodiglycol
either alone or with other glycols, alkylene oxides,
dicarboxylic acids, formaldehyde, amino-alcohols or
5 aminocarboxylic acids. Polycarbonate polyols which
may be used include products obtained by reacting
diols such as 1,3-propanediol, 1,4-butanediol, 1,6-
hexanediol, diethylene glycol or tetraethylene glycol
with diaryl carbonates, for example, diphenyl
10 carbonate, or with phosgene.

 Polyacetal polyols which may be used include
those prepared by reacting glycols such as diethylene
glycol, triethylene glycol or hexanediol with
formaldehyde. Suitable polyacetals may also be
15 prepared by polymerizing cyclic acetals.

 Suitable polyolefin polyols include hydroxy-
terminated butadiene homo- and copolymers and suitable
polysiloxane polyols include polydimethylsiloxane
diols and triols.

20 Other conventional polymeric polyols which
may be additionally present in the isocyanate reactive
composition include dispersions or solutions of
addition or condensation polymers in polyols of the
types described above. Such modified polyols, often
referred to as "polymer polyols" have been fully
25 described in the prior art and include products
obtained by the in situ polymerization of one or more
vinyl monomers, for example, styrene and/or
acrylonitrile, in polymeric polyols, for example
30 polyether polyols, or by the in situ reaction between

- 1 a polyisocyanate and an amino- and/or hydroxy-
functional compound, such as triethanolamine, in a
polymeric polyol. Polyoxyalkylene polyols containing
from 5 to 50% by weight of dispersed polymer are
5 particularly useful. Particle sizes of the dispersed
polymers of less than 50 microns are preferred.

The average molecular weight of these
additional conventional polymeric polyols preferably
range from 1000-8000 and most preferably from 1500-
10 7000; the hydroxyl value preferably ranges from 15-200
and most preferably from 20-100.

- The most preferred conventional polymeric
polyols that may additionally be present in the
isocyanate reactive mixture are polyoxyethylene
15 polyoxypropylene polyols having a number average
molecular weight of 2000 to 7000, an average nominal
functionality of 2-3 and an oxyethylene content of 10-
20% by weight, preferably having the oxyethylene
groups at the end of the polymer chain. These
20 additional polymeric polyols (i.e., polyol ethers) may
be present in the isocyanate reactive composition in
amounts up to 50% by weight thereof.

In the total polyol blend in the isocyanate
reactive composition, it is preferred that the
25 diol/triol ratio in the polymeric polyols ranges from
20/60 to 60/20, with the preferred ratio ranging from
about 30/50 to about 50/30.

Another component of the isocyanate reactive
composition is the chain-extending agent. Suitable
30 chain extenders will be evident to those skilled in

1 the art from the present disclosure. In general,
useful chain extenders are those having a formula
weight below about 750 and preferably from about 62 to
about 750. Suitable chain extenders have at least two
5 functional groups which contain active hydrogen atoms,
and include such examples as primary and secondary
diamines, amino alcohols, amino acids, hydroxy acids,
glycols and the like and mixtures thereof. It is
preferred that they have a functionality of two.
10 Preferred chain extenders are selected from polyols
such as ethylene glycol, diethylene glycol, 1,4-
butanediol, dipropylene glycol, and tripropylene
glycol; aliphatic and aromatic amines, e.g. 4,4'-
methylenedianilines having a lower alkyl (C₁-C₆)
15 substituent positioned on each N-atom, and the like.
Other chain extenders include primary and secondary
amines which react more readily with the
polyisocyanates utilized in the present invention than
does water. These include phenylenediamine,
20 ethylenediamine, diethylenetriamine, N-(2-
hydroxypropyl)- ethylenediamine, N,N'-di-(2-
hydroxylpropyl)- ethylenediamine, piperazine, 2-
methylpiperazine, and the like. Compounds such as
ethoxylated hydroquinone can also be employed as a
25 chain extending agent. In addition, fatty amines and
either amines can be employed as chain extending
agents. Examples of ether amines includes primary
ether amines of the formula
$$\text{ROCH}_2\text{CH}_2\text{CH}_2\text{NH}_2,$$

30 and ether diamines, such as

1 $\text{ROCH}_2\text{CH}_2\text{CH}_2\text{NH CH}_2\text{CH}_2\text{CH}_2\text{NH}_2,$

wherein R is alkyl containing 6-15 carbons, (both which are commercially available from TOMAH PRODUCTS); and ethoxylated amines of the formula:



wherein R_1 is alkyl group containing 10 to 26 carbon atoms, n is the total number of moles of ethylene oxide and is 2-15, and x is 1 to 14 (commercially available from TOMAH PRODUCTS). Other ether amines include tallow based fatty amines, such as tallow amines, tallow diamines, tallow triamines, tallow tetramines, hydrogenated tallow amine, tallow diamine dioleate and the like. These tallow based fatty amines are also commercially available from TOMAH PRODUCTS. The above-mentioned chain extending agents can be used singularly, in combination or in admixture with other chain extending agents including diethylene glycol, dipropylene glycol, ethanolamine, N-methyldiethanolamine, and N-ethyldiethanolamine, as well as adducts obtained by esterification of aliphatic carboxylic acids with aliphatic diols or triols such as those exemplified above utilizing from 0.01 to 1.08 mole of acid per mole of diol/triol. The preferred chain extending agents are 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, 1,4-cyclohexane diol, ethylene glycol, bishydroxyethoxybenzene, ethoxylated hydroquinone glycerine, and diethylene glycol either alone or in admixture.

1 The amount of chain extenders utilized will
have an effect on the physical properties of the skin
polyurethane foam. Therefore, in the present process
it is important to utilize the chain extender in the
5 amounts specified herein.

Generally, by increasing the amount of chain
extenders in the polyether system, a harder foam will
be produced. Without wishing to be bound, it is
believed that the chain extender introduces hard
10 segments into the elastomer. However, a significant
increase in hardness is generally accompanied by a
decrease in low temperature flexibility and a
reduction in fatigue resistance to the elastomer.
Without wishing to be bound, it is believed that the
15 decrease in these physical properties is attributable
to a decrease in the percentage of relatively long
chain (soft) segments in the elastomer. Other
disadvantages results if too much chain extender is
used; for example, compatibility of the polyol in the
20 isocyanate reactive composition and the chain extender
in the resin decreases with increasing amounts of the
short chain extender, thereby imposing significant
processing problems and limitations on such systems.
Moreover, bulk shipments and/or storage for even short
25 periods of time are not economically tolerable due to
the resulting phase separation of the polyol and the
chain extender. Even in use, processing requires
appropriate mixing to prevent phase separation.
Incompatibility of the system and/or marginal mixing
30 can adversely effect the physical properties of the

1 ultimate polyurethane foam products. As soon as the
reactant materials deviate appreciably from the
stoichiometric balance between hydroxy and isocyanate
ingredients, the resulting products, for example, shoe
5 soles, will crack during wear, making these articles
useless in commerce.

Although the amount of chain extender added
to the isocyanate reactive composition is dependent
upon the hardness requirement, to avoid the problems
10 described hereinabove, the inventor has found that the
chain extender be preferably present in amounts
ranging from about 6.0% to about 12.5% by weight of
the isocyanate reactive composition.

The blowing agent used according to the
15 present invention is water. It is the sole blowing
agent in the present process. Water reacts with
isocyanate groups generating nascent carbon dioxide
which then causes the polymer forming reaction mass to
expand and acquire a reduced density. For the purpose
20 of this invention, water is present in amounts
effective to result in the polyurethane foam having
the desired density as described herein. The amount
of water utilized is based upon the density
requirement of the shoe sole. Preferably, water is
25 present in the range of from about 0.25% to about
0.70% of the total weight of the isocyanate reactive
composition and more preferably from about 0.35% to
about 0.60% by weight of the total isocyanate reactive
composition.

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1 The inventor has found that the amount of
water used is related to the amount of chain extender
present. More specifically, he has found that when
the weight ratio of water to the chain extending agent
5 ranges from about 0.01 to about 0.20 and more
preferably from about 0.02 to about 0.09, polyurethane
foams having the requisite characteristics were
formed. This is a characteristic that makes the
present polyurethane foam quite unique from other
10 flexible foams since in most flexible foams, this
ratio is greater than 1 and usually greater than 10.
Thus, in flexible foams produced in the prior art, the
ratio is at least 5 times greater and usually one
order of magnitude greater than the ratio utilized in
15 preparing the reaction product of the present
invention.

 The present reaction system may further
comprise conventionally used additives, such as flame
retardants and catalysts, as needed for particular
20 applications. Useful flame retardants include
phosphonates, phosphites and phosphates, such as tris-
(2-chloroisopropyl) phosphate (TCPP), dimethyl methyl
phosphonate, ammonium polyphosphate and various cyclic
phosphates and phosphonate esters known in the art;
25 halogen-containing compounds known in the art, such as
brominated diphenyl ether and other brominated
aromatic compounds; melamine; antimony oxides, such as
antimony pentoxide and antimony trioxide; zinc
compounds such as zinc oxide; alumina trihydrate; and
30 magnesium compounds, such as magnesium hydroxide. The

1 flame retardants may be used in any suitable amount
which will be evident to those skilled in the art.
However, it is preferred that the flame retardant be
used in an amount of 0 to 55% of the isocyanate
5 reactive component of the present invention.

Useful catalysts include tertiary amines,
organometallic compounds and amides of saturated or
unsaturated C₁₂-C₂₄ fatty acids and di, tri or tetra-
aminoalkanes having at least one catalytic amino group
10 and at least one reactive amino group. Fatty amido-
amines having hydroxyl substituents may also be used.
A particularly preferred amido-amine compound is the
reaction product N,N-dimethyl propyl diamine and a
mixed fatty carboxylic acid available as BUSPERSE® 47
15 from Buckman Laboratories. Other preferred catalysts
are triethylene diamine, bis-(2-(N,N-
dimethylamino)ethyl) ether, and mixtures thereof.
Other catalysts which may be used include heterocyclic
amines and salts of tertiary amines (e.g., "delayed
20 action catalysts"). The catalysts are used in amounts
necessary for a particular application which will be
evident to one skilled in the art from the present
disclosure.

Other conventional additives generally used
25 in the art may also be used in the present invention.
Examples of suitable additives include fillers, such
as calcium carbonate, silica, mica, wollastonite, wood
flour, melamine, glass or mineral fibers, glass
spheres, etc.; pigments, such as carbon black;
30 surfactants; internal mold release agents; and

1 plasticizers. Such additives will be used in amounts
which will be evident to one skilled in the art from
the present disclosure.

5 Suitable surfactants include the diverse
silicone surfactants, preferably those which are block
copolymers of a polysiloxane and a polyoxyalkylene.
Exemplary of such surfactants are the products DC-193
and Q4-3667 available from Dow Corning and Tegostab
B4113 available from Goldschmidt. Other suitable
10 surfactants also include non-silicone containing
surfactants, such as poly(alkyleneoxides). When
present, the amount of surfactants advantageously
employed is from 0.1 to 2%, and preferably from 0.2%
to 1.3% of the total weight of the isocyanate reactive
15 composition.

 The polyurethanes are formulated and shaped
into molded objects by casting methods conventionally
known in the art, generally involving the use of a
casting machine. Examples of low pressure casting
20 machines include those offered commercially by
Klockner Ferromatik Desma, Inc., Erlanger, Kentucky,
including the DS 30/30 and PSA 91, while high pressure
models including machines made by Cannon Corp. may
also be used.

25 In the casting process, the polyisocyanate
composition is referred to as the "A" component and
the isocyanate reactive composition and water is
referred to as the "B" component. If additives are
employed, they are generally incorporated into the "B"
30 component, although they may also be added in the "A"

1 component so long as they are not isocyanate-reactive.
The "B" component mixture, including additives, may be
blended or agitated in a suitable container or supply
tank, generally in the range of about 20°C to about
5 50°C, although temperatures up to about 75°C may be
employed. Agitation can be conducted using
conventional propeller type stirrers (generally
supplied by the casting machine manufacturer) at RPM's
of several hundred at most.

10 The "A" and "B" components are placed in
separate containers, which are generally equipped with
agitators, of the casting machine wherein the
temperature of each component is about ambient to
about 70°C. Molded polyurethane products are made by
15 conducting each component via suitable metering pumps,
to a mixing head where the components are mixed under
low pressures, generally pressures less than about 30
bar, preferably less than about 20 bar. The mixed
components are then poured or injected into a mold.

20 Once a desired mold shape has been filled,
the mold is closed and curing is effected. Generally
curing temperatures of about 30°C to about 60°C are
used. Curing (as reflected by demold times) requires
about 1 to 30 minutes, usually about 3 to 10 minutes.
25 This cure time is ample to allow mixing, foaming if
desired, and mold filling, yet sufficiently rapid to
allow high rates of production.

The reaction of the "A" component and "B"
component to make the molded polyurethanes is carried
30 out at an isocyanate index between about 0.85 and

1 about 1.15, preferably between about 0.90 and about
1.05. Most preferably, the reaction is carried out at
an isocyanate index of about 0.95 to about 1.0 when
5 based on total active hydrogens available including
the water reaction.

The polyurethane foams prepared by the
present invention are not low density polyurethane
foams. The density of the product ranges from 0.1 to
about 1.1 spg, preferably from about 0.25 to 0.80 and
10 more preferably from 0.3 to about 0.75 spg. Unlike
low density polyurethane foams, the polyurethane foams
prepared by the present invention display excellent
mechanical characteristics, including abrasion
resistance, durability, stability and flexibility,
15 making them ideal for use as a shoe sole.

In the utilization of the present
invention(s) to manufacture integral skin
microcellular polyether elastomer articles, such as
shoe soles, an aspect which is highly preferred,
20 either of two commonly employed sole making processes
are satisfactory. In one process, the left and right
foot soles are cast as unit soles, removed from the
cast, and then attached to the shoe uppers by a
suitable adhesive. In the other process, the shoe
25 uppers, i.e., left and right foot, are presented as
one mold surface and the formulation is injected into
the mold cavity defined by the shoe uppers and the
mold walls. In either case, the molds are closed wall
molds so as to obtain the mold defined sole shape.
30 This sole shape may not necessarily be smooth and may

1 have built-in mold ridges such as for resiliency,
cushioning, lugs for slip resistance, etc.

5 In either process, the typical adhesives
(also called "cements") for attaching (also called
"cementing") the soles to the uppers are well known.
In the second process, i.e., the direct attachment,
the adhesive may be the cast polyurethane minus the
blowing agent which is cured with the cast foam as it
cures, or it may be a different polyurethane adhesive.

10 Unless stated to the contrary, all
percentages are weight percentages. In addition,
unless indicated to the contrary, all weights are in
grams.

The following examples further illustrate
15 the invention.

In the examples, the following formulations
and reaction components are referenced:

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1	Daltocel [®] F459	Polyether diol having a 20.7% ethylene oxide (EO) cap and an equivalent weight of 1870.
5	Daltocel [®] F435	Polyether polyoxypropylene triol having a 16.4% EO cap and an equivalent weight of 1600.
	Arcol [®] 2580	Polyether polyol, random copolymer of ethylene oxide and propylene oxide containing 75% EO. Equivalent weight=1336, OH#-42
10	Dabco [®] EG	Triethylene diamine in ethylene glycol
	Niax [®] A1	Tertiary amine catalyst (dimethylamino diethyl ether in dipropylene glycol, ratio 1/3 w/w)
	Dabco [®] 1027	Heterocyclic amine catalyst in ethylene glycol
15	IX 193	Silicone surfactant
	LI 412T	Silicone-type internal mold release agent (mixture of amino functional polyether polysiloxanes) OH #=25
20	Suprasec [®] 2433	54.3% Pure MDI (97.5% 4,4'-MDI/2.5% 2,4'-MDI) 39.7% Daltocel F481 (ethylene oxide capped diol) EO content = 27.1% Equivalent Wgt=1870 6.0% Suprasec [®] 2020 (uretonimine-modified MDI)
25	Arcol [®] 34-28	Polyether triol having a 15% ethylene oxide (EO) capped and 20% polymer dispersion (10% acrylonitrile and 10% styrene) having an equivalent of about 2,000 and OH#=28.
	Daltocel [®] F481	Polyether capped diol of equivalent wt. 1870, having 27.1% EO (remainder PO).

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Example 1

In this example, a polyurethane foam was prepared by mixing the prepolymer (Suprasec[®] 2433) with the isocyanate reactive composition in the presence of water in a low pressure casting machine (DS 30/30 or PSA 91, both of which are sold by Klockner Ferromatik Desma, Inc.) in accordance with the procedure described herein. The amounts of each component utilized are tabulated hereinbelow by weight:

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Component	% (w/w)
A. Polyisocyanate	
1. Suprasec [®] 2433	71%
B. Isocyanate Reactive Component	
1. Daltocel [®] F-435	31.64
2. Arcol [®] 34-28	10.0
3. Datlocel [®] F-481	44.72
4. Arcol [®] 2580	3.0
5. Ethylene glycol	6.0
6. Dabco [®] GG	1.8
7. NIAX [®] A1	0.3
8. Dabco [®] 1027	0.3
9. DC 193	0.3
10. LI 412T	1.5
Component	
C. H ₂ O	0.44

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1 More specifically, Suprasec®2433 was
prepared by placing substantially pure MDI (54.3
Kg./100 Kg. Suprasec®2433) comprised of a mixture of
97.5% 4,4'-MDI and 2.5% 2,4'-MDI into a reaction vessel
5 at 40°C. The temperature of the reaction vessel was
raised to 80°C and Daltocel®F481 (39.7 Kg./100 Kg.
Suprasec® 2433) was added. The mixture was stirred at
80°C for 2½ hours, at which time the NCO content of
the mixture was determined to be in the range of
10 18.25-18.65%. Suprasec® 2020 (6 Kg./100 Kg. Suprasec®
2433) was added to the reaction mixture at 80°C and it
was allowed to mix for 30 minutes. The reaction
mixture was then allowed to cool to room temperature,
and the final NCO content was found to be between
15 18.90%-19.3%. The contents were placed in a container
of a low pressure casting machine equipped with an
agitator and temperature control system to control the
components temperature in the range of 5°C-70°C.

Component B consisting of the isocyanate
20 reactive components and water in the amounts listed
hereinabove were mixed at room temperature in a second
container of the casting machine equipped with an
agitator and temperature control system to control the
components temperature in the range of 5°C-70°C. The
25 molded polyurethane product was made by conducting
each component in the weight ratio indicated
hereinabove via suitable pumps of the casting machine
into the mixing head wherein the components are mixed
under low pressures, the pressure being less than 20
30 bar. The mixture of the two components were next

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- 1 casted into the appropriate mold of Style A or Style B shoe style (see Figures 1-2).

5 Once the desired mold shape was filled, the mold was closed, and curing was effected at a curing temperature of 30-60° for about 3 to 10 minutes, and the shoe sole of Style A or B comprised of polyurethane foam was formed.

10 The polyurethane foam was molded into a shoe sole of either style A or B (see Figures 1 and 2, respectively) using the appropriate shoe mold. "Free Time" Style Mold of San Antonio Shoes Company was used for the preparation of the A style shoe sole and "Bounce" Style mold of Wolverine World Wide Co. was used for the B style shoe sole.

15 Figure 1 depicts the style A shoe sole (1). The SAS on the lower sole component half (5) identifies it as the San Antonio Shoe Style. The shoe sole contains a pattern of indentations (2) in the upper sole component half (forefoot) and the lower sole component half. The thickness of the sole is
20 relatively thin; it is 5/16". Various channels (3) are present in both the forefoot and the lower sole. The depth of the grooves is less than 1/16". These grooves have rounded corners, and they do not form a straight
25 line. If shoe cracking occurs, it occurs in the area designed as (4).

 Figure 2 depicts the style B shoe sole (6). This shoe style is quite distinct from that of shoe style A. The forefoot (7) is relatively thick; the thickness thereof is equal to 1/2" or
30 greater. The forefoot contains a pattern consisting

1 of channels forming grooves (6) with the depth of
these grooves being $3/32$ " thick. Unlike the grooves
in style A, these grooves form a straight line across
the forefoot. Furthermore, they form square-like
5 corners, instead of the rounded corners in style A.

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Comparative Examples 1-3

Comparative Example 1 is a traditional formulation for preparing a polyurethane using polyether polyol having a EO content of less than 25% by weight.

Comparative Examples 2 and 3 describe two formulations in which only 1 type of polyether polyol of high EO content is utilized. In comparative Example 2, only the high ethylene oxide polyether polyol was utilized in the absence of the random EO/PO copolymer, while in Comparative Example 3, the random EO/PO copolymer was utilized but in the absence of the high ethylene oxide polyether polyol. The various formulations were prepared in accordance with the procedure described in Example 1 wherein the Suprasec[®] 2433 was mixed with the polyether polyol in a casting machine and then molded into the appropriate shoe style. The formulations in Comparative Examples 1-3 are tabulated hereinbelow.

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1 Formulation for Comparative Examples 1-3

	Component	Wt %		
		Comparative Example 1	Comparative Example 2	Comparative Example 3
5	1. Polyisocyanate Suprasec 2433	71	71	71
	2. Isocyanate Reactive Component			
10	1. Daltocel® F459	44.72	44.72	0
	2. Daltocel® F435	34.64	31.64	34.64
	3. Arcol® 34-28	10.0	10.0	10.0
	4. Daltocel® F-481	0	0	44.72
15	5. Arcol® 2580	0	3	0
	6. Ethylene Glycol	6.0	6.0	6.0
	7. Dabco® EG	1.8	1.8	1.8
	8. Niax® A1	0.3	0.3	0.3
20	9. Dabco® 1027	0.3	0.3	0.3
	10. DC 193	0.3	0.3	0.3
	11. LI 412T	1.5	1.5	1.5
	3. H ₂ O	0.44	0.44	0.44

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Example 2

This example compares the flexible fatigue of the shoe sole prepared from the polyurethane foam of Example 1 and the comparative examples.

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- 1 polyurethane produced in Example 1 and comparative
examples 1-3 were compared utilizing a standard test
known as Bata Belt Flex test, as described in
"Physical Test Method", published by SATRA Footwear
5 Technology Center, February 1989, pp. 1-9, the
contents of which are incorporated by reference. The
sample is placed on a belt flexing machine
manufactured by Satra Footwear Technology Center,
Kettering North-Hamptonshire, England which subjects
10 the forefoot of the sole to flexing stress. Thus,
this test measures the ability of the shoe style
prepared from the polyurethane foam to withstand
cracking as a result of the millions of cycles of
bending to which each shoe sole is subjected.
- 15 The relationship of the results of Bata Belt
Flex and risk of fatigue cracking is listed in the
following table I:

TABLE I

Bata Belt Flex, kcs	Risk of Fatigue Cracking
Less than 5	Very high
5-15	High
15-35	Medium
35-50	Low

- 20 The results of the Bata Belt Flex test on
the various shoe soles prepared from the polyurethane
foam produced in Example 1 and the Comparative
examples set forth in Table II are tabulated
hereinbelow:
- 25
- 30
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TABLR II

Flex Fatigue Property	2. Comparative Example 1			3. Comparative Example 2			4. Comparative Example 3			5. Comparative Example 4		
	A	B	C	A	B	C	A	B	C	A	B	C
Shoe sole density, g/cc	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3
Style	1	2	3	4	5	6	7	8	9	10	11	12
Bata belt flex, kcs	35-40	10-15	15-20	20-25	25-30	30-35	35-40	40-45	45-50	50-55	55-60	60-65

- 1 As shown by the data in the table, for the soles
comprised of the polyurethane prepared in Comparative
Examples 1-3, the Bata belt flex values were
significantly lower than that of the soles made from
5 the polyurethane foam prepared in accordance with the
present invention (i.e., Example 1).

These results show that there is a marked
and significant improvement in the Bata belt flex
property when the shoe sole was prepared from the
10 polyurethane of the present invention. The data
accurately reflect that the combination of the two
high ethylene oxide polyether polyols in the
isocyanate reactive component provides a synergistic
effect. The flex fatigue performance of the
15 polyurethane produced when both polyols were present
was significantly improved, i.e., the shoe soles
became significantly more flexible relative to the
shoe soles comprised of a polyurethane foam prepared
from the isocyanate composition containing either one
20 (Comparative Example 2, 3) or neither (Comparative
Example 1) polyol.

The above preferred embodiments and examples
were given to illustrate the scope and spirit of the
present inventor. These embodiments and examples will
25 make apparent to those skilled in the art other
embodiments and examples. The other embodiments and
examples are within the contemplation of the present
invention. Therefore, the present invention should be
limited only by the appended claims.

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1. WHAT IS CLAIMED IS:

1. A flexible integral skin polyurethane foam prepared by intimately contacting under effective reaction conditions a polyisocyanate composition with an isocyanate reactive composition in the presence of a water blowing agent, wherein

(a) the polyisocyanate composition has a free NCO value of about 15% to about 25% by weight and comprises an isocyanate terminated prepolymer prepared from the reaction of an excess of organic polyisocyanate and a first ethylene oxide capped polymer polyol having an average nominal hydroxyl functionality of 2-6, an equivalent weight ranging from about 700 to about 5,000 and an ethylene oxide content of at least about 25% by weight, whereby at least 50% of the ethylene oxide group is present at the end of the polyether polyol;

(b) the isocyanate reactive composition comprises a chain extending agent that is present in amounts ranging from about 6.0% to about 12.5% by weight, and a mixture of a second ethylene oxide capped polyether polyol and a random copolymer of ethylene oxide and propylene oxide in synergistically effective amounts to form said polyurethane foam, said second ethylene oxide capped polyol having an average nominal hydroxyl functionality of 2-3, an equivalent weight ranging from about 700 to about 5000 and an ethylene oxide content of at least weight 25% by weight thereof wherein at least about 50% of the ethylene oxide group being present at the end of the

1 polyether polyol and said copolymer having an average
nominal hydroxyl functionality of 2-3, an equivalent
weight ranging from about 700 to about 5000 and an
ethylene oxide content of at least about 60% by
5 weight; and

(c) water, as the sole blowing agent present
in an amount effective to provide the resulting
polyurethane with a density ranging from about 0.1 to
about 1.1 sp.gr, wherein the weight ratio of water to
10 the chain extending agent ranges from about 0.01 to
about 0.20.

2. The polyurethane foam of Claim 1 wherein
said isocyanate reactive composition contains a diol
and a triol, the diol/triol weight ratio ranging from
15 about 1:3 to about 3:1.

3. The polyurethane foam of Claim 1 wherein
the second ethylene oxide capped polyol is present in
said mixture in an amount ranging from about 20% to
about 80% by weight of the isocyanate reactive
20 composition and the copolymer is present in an amount
ranging from about 1.5% to about 23% by weight of the
isocyanate reactive composition.

4. The polyurethane foam of Claim 3 wherein
the second ethylene oxide capped polyether polyol is
25 present in an amount ranging from about 40% to about
60% by weight of the isocyanate reactive composition.

5. The polyurethane foam of Claim 3 wherein
the copolymer is present in an amount ranging from
about 2% to about 5% by weight of the isocyanate
30 reactive composition.

1 6. The polyurethane foam of Claim 1 wherein
the ethylene oxide content of the second ethylene
oxide capped polyol ranges from about 25% to about 35%
by weight thereof and the ethylene oxide content of
5 the copolymer ranges from about 60% to about 85% by
weight thereof.

 7. The polyurethane foam of Claim 1 wherein
the equivalent weight of the second ethylene oxide
capped polyol ranges from about 1,000 to about 3,000.
10 8. The polyurethane foam of Claim 7 wherein
the equivalent weight of the second ethylene oxide
capped polyol ranges from about 1,200 to about 2,000.

 9. The polyurethane foam of Claim 1 wherein
the equivalent weight of the copolymer ranges from
15 about 1,000 to about 3,000.

 10. The polyurethane foam of Claim 9
wherein the equivalent weight of the copolymer ranges
from about 1,200 to about 2,000.

 11. The polyurethane foam of Claim 1
20 wherein water is present in an amount ranging from
about 0.25% to about 0.70% by weight of the isocyanate
reactive composition.

 12. The polyurethane foam of Claim 1
wherein the weight ratio of water to the chain
25 extending agent ranges from about 0.02 to about 0.09.

 13. The polyurethane foam of Claim 1
wherein the density thereof ranges from about 0.25 to
about 0.80 sp gr.

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1 14. The polyurethane foam of Claim 13
wherein the density thereof ranges from about 0.30 to
about 0.75 sp. gr.

5 15. The polyurethane foam of Claim 1
wherein the polyisocyanate composition is reacted with
the isocyanate reactive composition in a weight ratio
ranging from about 0.4 to about 2.5.

10 16. The polyurethane foam of Claim 1
wherein the polyisocyanate composition has a free NCO
value of about 17% to about 21% the first polyether
polyol has an average nominal hydroxyl functionality
of 2-4, an equivalent weight of about 1,000 to about
3,000 and has an ethylene oxide content ranging from
about 25% to about 35% by weight thereof, and the
15 organic polyisocyanate used for preparing the
prepolymer is a diphenylmethane diisocyanate based
polyisocyanate.

20 17. The polyurethane foam of Claim 16
wherein said prepolymer is prepared from the reaction
of an excess amount of phenylmethanediisocyanate based
polyisocyanate and said polyol, wherein said
diphenylmethane diisocyanate contains about 5% to
about 15% by weight MDI variant, greater than about
85% by weight 4,4' MDI and less than about 5% by
25 weight 2,4'-MDI.

30 18. The polyurethane foam of Claim 16
wherein said phenylmethane diisocyanate based
polyisocyanate contains at least 85% by weight of
4,4'-MDI or a variant thereof.

- 1 19. The polyurethane foam of Claim 1
wherein at least about 90% of the groups on the
prepolymer formed by reacting the polyisocyanate and
the polyol are urethane groups.
- 5 20. A process for preparing a flexible
polyurethane foam comprising contacting under
effective reaction conditions a polyisocyanate
composition with an isocyanate reactive composition in
the presence of water as the sole blowing agent,
10 wherein
 (a) the polyisocyanate composition has a
free NCO value of about 15 to about 25% by weight and
comprises an isocyanate terminated prepolymer prepared
from the reaction of an excess of organic
15 polyisocyanate and a first ethylene oxide capped
polymer polyol having an average nominal hydroxyl
functionality of 2-6, an equivalent weight ranging
from about 700 to about 5,000 and an ethylene oxide
content of at least about 25% by weight whereby at
20 least 50% of the ethylene oxide group is present at
the end of the polyether polyol;
 (b) the isocyanate reactive composition
comprises a chain extending agent that is present in
amounts ranging from about 7.0% to about 12.5% by
25 weight, and a synergistically effective amount of a
mixture of a second ethylene oxide capped polyether
polyol and a random copolymer of ethylene oxide and
propylene oxide to form said polyurethane foam
polyurethane foam, said second ethylene oxide capped
30 polyol having an average nominal hydroxyl

- 1 functionality of 2-3, an equivalent weight ranging
from about 700 to about 5000 and an ethylene oxide
content of at least weight 25% by weight thereof
wherein at least about 50% of the ethylene oxide group
5 is present at the end of the polyether polyol and said
copolymer has an average nominal hydroxyl
functionality of 2-3, an equivalent weight ranging
from about 700 to about 5000 and an ethylene oxide
content of at least about 60% by weight; and
10 (c) water, as a sole blowing agent, present
in an amount effective to provide the resulting
polyurethane with a density ranging from about 0.1 to
about 1.1 sp. gr, wherein the weight ratio of water to
the chain extending agent ranges from about 0.01 to
15 about 0.20.

21. The process of Claim 20 wherein said
isocyanate reactive composition contains a diol and a
triol, the diol/triol weight ratio ranging from about
1:3 to about 3:1.

- 20 22. The process of Claim 20 wherein the
second ethylene oxide capped polyol is present in said
mixture in an amount ranging from about 20% to about
80% by weight of the isocyanate reactive composition
and the copolymer is present in an amount ranging from
25 about 1.5% to about 23% by weight.

23. The process of Claim 22 wherein the
polyol is present in an amount ranging from about 40%
to about 60% by weight of the isocyanate reactive
composition.

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1 24. The process of Claim 22 wherein the
copolymer is present in an amount ranging from about
2% to about 5% by weight of the isocyanate reactive
composition.

5 25. The process of Claim 20 wherein the
ethylene oxide content of the second ethylene oxide
capped polyol ranges from about 25% to about 35% by
weight thereof and the ethylene oxide content of the
copolymer ranges from about 60% to about 85% by weight
10 thereof.

 26. The process of Claim 20 wherein the
equivalent weight of the second ethylene oxide capped
polyol ranges from about 1,000 to about 3,000.

15 27. The process of Claim 26 wherein the
equivalent weight of the second ethylene oxide capped
ranges from about 1,200 to about 2,000.

 28. The process of Claim 20 wherein the
equivalent weight of the copolymer ranges from about
1,000 to about 3,000.

20 29. The process of Claim 28 wherein the
equivalent weight of the copolymer ranges from about
1,200 to about 2,000.

 30. The process of Claim 20 wherein water
is present in an amount ranging from about 0.25 to
25 about 0.70% by weight of the isocyanate reaction
composition.

 31. The process of Claim 20 wherein the
weight ratio of water to the chain extending agent
ranges from about 0.02 to about 0.09.

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1 32. The process of Claim 20 wherein the
density thereof ranges from about 0.25 to about 0.80
sp. gr.

5 33. The process of Claim 32 wherein the
density thereof ranges from about 0.30 to about 0.75
sp. gr.

10 34. The process of Claim 20 wherein the
polyisocyanate composition is reacted with the
isocyanate reaction composition in a weight ratio
ranging from about 0.3 to about 3.0.

15 35. The process of Claim 20 wherein the
polyisocyanate composition has a free NCO value of
about 17 to about 21% by weight, the polyether polyol
has an average nominal hydroxyl functionality of 2-4,
an equivalent weight of about 1,000 to about 3,000 and
an ethylene oxide content ranging from about 25% to
about 35% by weight thereof, and the organic
polyisocyanate used for preparing the prepolymer is a
diphenylmethanediisocyanate based polyisocyanate.

20 36. The process of Claim 35 wherein said
prepolymer is prepared from an excess amount of a
phenyl methane diisocyanate based polyisocyanate and
said polyol, wherein said phenylmethanediisocyanate
based polyisocyanate contains about 5% to about 15% by
25 weight MDI variant, greater than about 85% by weight
4,4'-MDI and less than about 5% by weight 2,4'-MDI.

30 37. The process of Claim 35 wherein said
phenylmethane diisocyanate based polyisocyanate
contains at least 85% by weight of 4,4'-MDI or a
variant thereof.

1 38. The process of Claim 20 wherein at least
about 90% of the groups on the prepolymer formed by
reacting the polyisocyanate and the first polyol are
urethane groups.

5 39. A reaction system comprising
 (a) a polyisocyanate composition comprising
an isocyanate terminated prepolymer prepared by
reciting an excess of organic polyisocyanate and a
first ethylene oxide capped polyether polyol having an
10 average nominal hydroxyl functionality of 2-6, an
equivalent weight ranging from about 700 to about
5,000, and an ethylene oxide content of at least about
25% by weight, whereby at least 50% of the ethylene
oxide group is present at the end of the polyether
15 polyol,

 (b) an isocyanate reactive composition
comprising a chain extending agent that is present in
amounts ranging from about 6.0% to about 12.5% by
weight, and a mixture of a second ethylene oxide
20 capped polyether polyol and a random copolymer of
ethylene polyols and a random copolymer of ethylene
oxide and propylene oxide, said second ethylene oxide
capped polyol having an average nominal hydroxyl
functionality of 2-3, an equivalent weight ranging
25 from about 700 to about 5,000 and an ethylene oxide
content of at least about 25% by weight thereof,
wherein at least about 50% of the ethylene oxide group
thereof is present at the end of the polyether polyol,
and said copolymer having an average nominal hydroxyl
30 functionality of 2-3, an equivalent weight ranging

1 from about 700 to about 5,000 in an ethylene oxide
content of at least about 60% by weight; and

(c) water,

5 wherein the free NCO value of the
polyisocyanate composition ranges from about 15% to
about 25%, and wherein the weight ratio of water to
the chain extending agent ranges from about 0.01 to
about 0.20.

40. The reaction system according to Claim
10 39 wherein the weight ratio of the polyisocyanate
composition to isocyanate reactive composition ranges
from about 0.4 to about 2.5.

41. The reaction system according to Claim
39 wherein the weight ratio of water to the chain
15 extending agent range from about 0.02 to about 0.09.

42. The reaction system according to Claim
39 wherein the polyisocyanate composition has a NCO
value of about 17% to about 21%.

43. The reaction system according to Claim
20 39 wherein the polyisocyanate composition has a NCO
value of about 17% to about 31%, the first polyether
polyol has an average nominal hydroxyl functionality
of 2-4, an equivalent weight of about 1,000 to about
3,000 and has an ethylene oxide content ranging from
25 about 25% to about 35% by weight thereof, and the
organic polyisocyanate is a diphenylmethane
diisocyanate based polyisocyanate.

44. The reaction system according to Claim
43 wherein said diphenylmethane diisocyanate contains
30 about 5% to about 15% by weight MDI variant, greater

1 than about 85% by weight 4,4'-MDI and less than 5% by weight 2,4'-MDI.

45. The reaction system according to Claim 43 wherein said diphenylmethane diisocyanate based polyisocyanate contains at least 85% by weight of 4,4'-MDI or a variant thereof.

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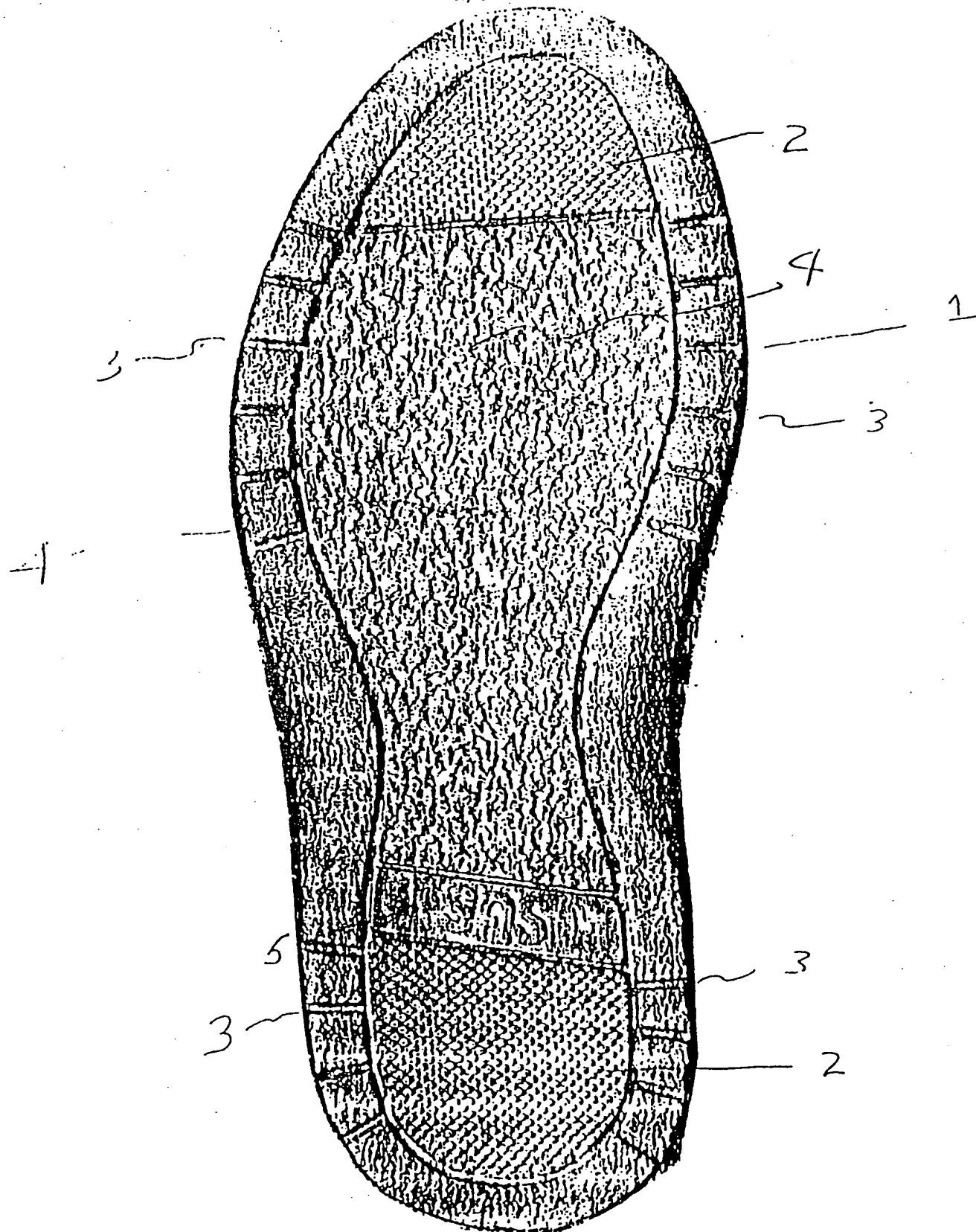


FIGURE 1.

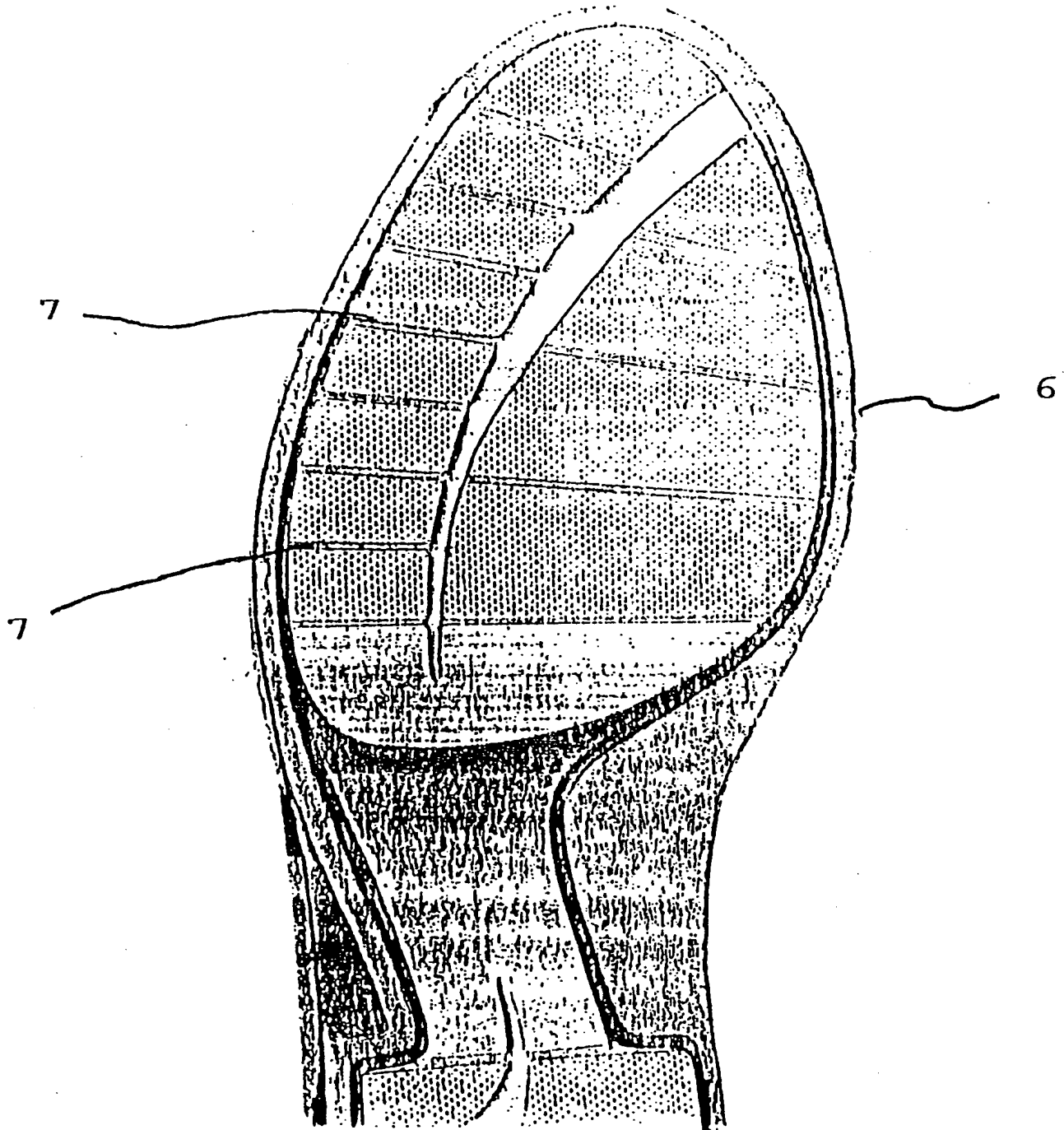


FIGURE 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 98/04315

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G18/10 C08G18/66 C08G18/48 //(C08G18/10,101:00),
(C08G18/66,101:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 420 273 A (DOW CHEMICAL CO) 3 April 1991 see claims 1-10 see page 3, line 12 - page 4, line 30 see table 3A	1
A	EP 0 497 492 A (ICI PLC) 5 August 1992 see claims 1,8,9 see page 3, line 12 - line 48	1
A	US 4 559 366 A (HOSTETTLER FRITZ) 17 December 1985 see claims 1,2,5	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

18 November 1998

Date of mailing of the international search report

26/11/1998

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 98/04315

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